



Short communication

Activation of sulfur active material in an all-solid-state lithium–sulfur battery



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HIGHLIGHTS

- Sulfur content was 50 wt% in positive composite electrode.
- A P/S ratio in solid electrolyte was correlated with sulfur's reactivity.
- Influence of sulfur's reactivity was larger than ionic conductivity of electrolyte.
- Discharge capacity of 1096 mAh g⁻¹ was obtained at 6.4 mA cm⁻².

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ABSTRACT

Charge–discharge performance of all-solid-state Li/S batteries using several solid electrolytes to enhance energy density is investigated at 25 °C. The sulfur content in the positive composite electrode is 50 wt%. A correlation between the P/S ratio in a solid electrolyte and the reactivity of sulfur is observed. The capacity of a positive composite electrode using a Li_{1.5}PS_{3.3}{60Li₂S–40P₂S₅(mol%)} electrolyte is 1096 mAh g⁻¹ under 6.4 mA cm⁻² at 25 °C. This value is much higher than the capacity for a Li_{4.0}P–S_{4.5}{80Li₂S–20P₂S₅} electrolyte (565 mAh g⁻¹), although the ionic conductivity of Li_{1.5}PS_{3.3} was lower than Li_{4.0}PS_{4.5} (2×10^{-5} S cm⁻¹, 5×10^{-4} S cm⁻¹, respectively).

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1. Introduction

The demand for energy storage devices has been increasing because of energy shortages and growing concerns about global warming. Rechargeable lithium ion batteries are important devices for portable equipments, and they have recently attracted significant attention as power sources for electric vehicles and hybrid electric vehicles. However, batteries for such large-scale power applications require larger energy density than that of currently used batteries. Therefore, there is a strong need to upgrade the energy density of rechargeable lithium batteries. Elemental sulfur is one of the most promising positive electrode materials because of its high theoretical specific capacity (1672 mAh g⁻¹) [1,2]. However, utilization of a sulfur electrode is not sufficient to achieve the

theoretical capacity, and rapid capacity fading is observed upon cycling of Li/S batteries using conventional organic liquid electrolytes [3]. This fading is caused by the high solubility of polysulfides formed during battery operation in liquid electrolytes.

Many researchers have focused on confining the sulfur materials in porous nanostructures to prevent the dissolution of lithium polysulfides during charge–discharge reactions [4]. According to their research, the cycle life and the utilization efficiency of sulfur in Li/S batteries were drastically improved by maintaining an electron conducting path to the sulfur active materials and physically inhibiting dissolution of polysulfides in liquid electrolytes. However, soluble species that escape from the matrix nanostructures over numerous cycles still exist, which results in consecutive capacity fading. The use of an inorganic solid electrolyte (SE) rather than an organic liquid electrolyte is an effective approach to inhibit the dissolution of lithium polysulfides. There are various inorganic SEs such as Li₂S–SiS₂, Li₂S–P₂S₅, and Li₄GeS₄–Li₃PS₄ systems that have high Li ion conductivities, i.e., $>10^{-4}$ S cm⁻¹ at 25 °C [5–8]. These SEs have been investigated as potential

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electrolytes in all-solid-state Li/S batteries. Li/S cells using these SEs indicate excellent cycling performance because polysulfide dissolution is completely inhibited [9–11].

Many reports focusing on high-capacity Li/S batteries using inorganic SEs have also been published. In these studies, the cells indicated high capacities per gram of sulfur; however, the sulfur content in the positive electrodes was still insufficient or the electrode was too thinly layered for practical use [12]. Therefore, the energy densities were relatively low. Because of the low electro and ionic conductivities of sulfur, maintaining high sulfur utilization efficiency became more difficult as the sulfur content increased. In addition, sulfur's low reactivity was another reason. In almost all studies, a great effort was made to improve all-solid-state Li/S battery performance by increasing the electron conductive path to sulfur and improving the ionic conductivity of SEs, whereas very few trials to improve the reactivity of sulfur itself have been performed. Therefore, we investigated improvement of all-solid-state Li/S battery performance focusing on the reactivity of sulfur. We found a correlation between the P/S ratio in a solid electrolyte and the reactivity of sulfur. When the P/S ratio was higher, activity of sulfur in a positive composite electrode increased and the capacity of sulfur decreased. We successfully demonstrated a new strategy to create a high-performance all-solid-state Li/S batteries using high P/S ratio SEs.

2. Experimental

Several positive composite electrode materials with elemental sulfur as an active material were prepared by ball milling with a planetary ball mill apparatus (Fritsch Pulverisette 7) under Ar atmosphere [9]. The weight ratio of sulfur (Aldrich, 99.5%), Ketjen-black (KB, Lion Co.), and SE was fixed at 50:10:40 in the positive composite electrode.

Reagent grade Li_2S (Furuuchi Chem., 99.9%), P_2S_5 (Aldrich, 99%), sulfur (Aldrich, 99.5%) and phosphorus red (Aldrich, 99.9%) were used as starting materials. SE was prepared by a mechanochemical method using a planetary ball mill apparatus [8]. The mechanochemical treatment using a ZrO_2 pot and balls was performed for the mixture of Li_2S and P_2S_5 (molar ratios = 80:20, 60:40, 40:60, and 20:80). Similarly, the mechanochemical treatment was performed for the mixture of Li_2S , sulfur, and phosphorus red (molar ratios = 0.8:2.0:3.2, 1.5:2.0:1.5, and 1.2:2.0:1.4). For a few of the SEs, a small Li_2S peak was observed by X-ray diffraction (XRD) (measured by Ultima 4; Rigaku Co.); other peaks were not observed (Fig. S1). Therefore, it can be considered that all SEs were almost amorphous. The ionic conductivities of the SEs at 25 °C were measured by an impedance analyzer (Cell Test System 1400, Solartron Analytical); measurement results are shown in Table 1.

The electrochemical properties of the positive composite electrodes were investigated in an all-solid-state cell [13]. Two-electrode cells were assembled in a glove box filled with dry Ar using several composite electrodes as the positive electrode, Li–In

alloys as the negative electrode, and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ [7] as the solid electrolyte.

The positive electrode powder (7.5 mg) and the solid electrolyte powder (70 mg) were placed in a polycarbonate tube (diameter = 10 mm) and pressed under 200 MPa to form a two-layered pellet. The negative electrode, which was formed by superimposing a lithium foil on an indium foil, was placed on the surface of the two-layered pellet such that the superimposed foils were in contact with the solid electrolyte. In this process, the Li and In foils formed a Li–In alloy layer. Then, the resulting three-layered pellet was sandwiched by two stainless steel rods acting as current collectors. The molar ratio of Li/In was 0.79 in the negative electrode. When the molar ratio was less than 1, the potential of Li–In alloys has been reported to be constant at approximately 0.6 V vs. Li [14]. Here, 0.6 was adopted as the value for the potential difference between Li–In and Li.

Electrochemical tests were conducted at several constant current densities from 0.64 to 6.4 mA cm^{-2} at 25 °C in Ar atmosphere using a charge–discharge measuring device, ACD-01 (Asuka Electronics Co. Ltd.).

3. Results and discussion

Fig. 1 shows the charge–discharge curves of the all-solid-state Li/S cells using several positive composite electrodes at 0.64 mA cm^{-2} , which corresponds to 0.08 C (1 C = 1672 mA g^{-1} sulfur). The cells were charged to 2.5 V and discharged to 0.5 V (vs. Li–In). All cells act as a secondary battery. In general, in the early period of discharge, the reaction proceeds primarily near the interfacial surface between the SE and positive composite electrode; consequently, lithium ions do not have to be carried a significant distance. In other words, in a positive composite electrode, the contribution that the reactivity of sulfur makes to the progress of reaction is much larger than that of ionic conductivity. Therefore, we consider that the reactivity of sulfur in a positive composite electrode can be estimated by comparing discharge potential values in the early period of discharge, e.g., at 100 mAh g^{-1} . In Fig. 1, the cell potential in the early discharge period increases as the P/S ratio of the SE is increased. The discharge potentials at 100 mAh g^{-1} for the P/S ratios of the SEs in the positive composite electrodes are plotted in Fig. 2 and listed in Table 1. From Fig. 2, it is evident that the discharge potential at

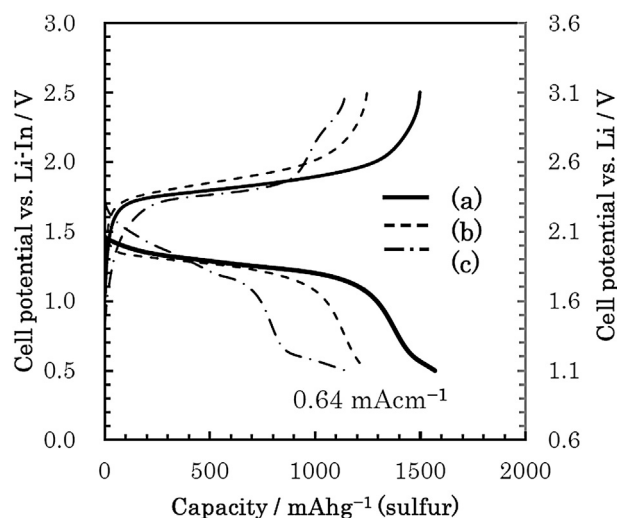


Fig. 1. Charge–discharge curves of the all-solid-state Li/S cells with positive composite electrodes using (a) $\text{Li}_{1.5}\text{PS}_{3.3}$, (b) $\text{Li}_{4.0}\text{PS}_{4.5}$, and (c) $\text{Li}_{1.2}\text{PS}_{1.3}$ under 0.64 mA cm^{-2} at 25 °C.

Table 1
Ionic conductivities of various solid electrolyte (SE).

Chemical formula	Reagent ratio	P/S ratio	Ionic conductivity at 25 °C (mS cm^{-1})
$\text{Li}_{4.0}\text{PS}_{4.5}$	$\text{Li}_2\text{S}:\text{P}_2\text{S}_5 = 80:20$	0.222	0.483
$\text{Li}_{1.5}\text{PS}_{3.3}$	$\text{Li}_2\text{S}:\text{P}_2\text{S}_5 = 60:40$	0.308	0.021
$\text{Li}_{0.7}\text{PS}_{2.8}$	$\text{Li}_2\text{S}:\text{P}_2\text{S}_5 = 40:60$	0.353	<0.001
$\text{Li}_{0.3}\text{PS}_{2.6}$	$\text{Li}_2\text{S}:\text{P}_2\text{S}_5 = 20:80$	0.381	<0.001
$\text{Li}_{0.8}\text{PS}_{2.0}$	$\text{Li}_2\text{S}:\text{P}:\text{S} = 0.8:2.0:3.2$	0.500	<0.001
$\text{Li}_{1.5}\text{PS}_{1.5}$	$\text{Li}_2\text{S}:\text{P}:\text{S} = 1.5:2.0:1.5$	0.667	0.033
$\text{Li}_{1.2}\text{PS}_{1.3}$	$\text{Li}_2\text{S}:\text{P}:\text{S} = 1.2:2.0:1.4$	0.769	0.033

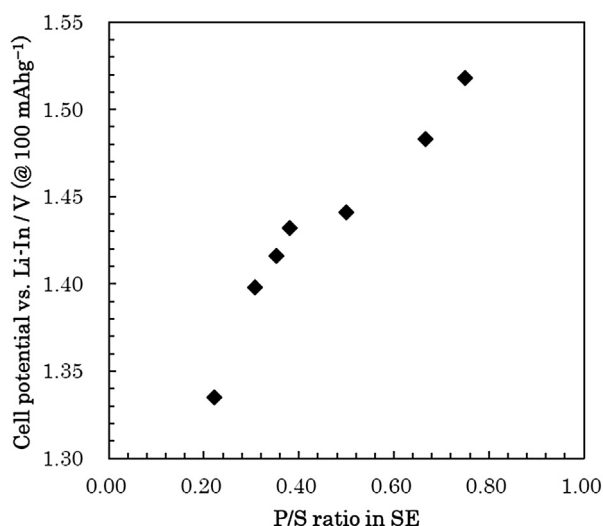


Fig. 2. Plot of the discharge potentials at 100 mAh g⁻¹ for various P/S ratios in solid electrolyte (SE).

100 mAh g⁻¹ increases as the P/S ratio in the SEs is increased, which indicates that sulfur is more activated.

Fig. 3 shows the discharge curve of the all-solid-state Li/S cell for a positive composite electrode using Li_{1.2}PS_{1.3} at 0.64 mA cm⁻². The discharge curve has an inflection point, which is defined as the intersection of two tangents, at approximately 0.6 V (vs. Li-In). In this study, capacity from 0 to the inflection point is denoted as “Capacity A” and that from the inflection point to the end point is denoted as “Capacity B”. Capacity A is considered to be generated by the reaction of S → Li₂S from the perspective of operating potential. On the other hand, the reaction that generates Capacity B has not yet been elucidated. It is known that phosphorus active material operates near the potential [15]; however, from the X-ray photoelectron spectroscopy (XPS) spectra (measured by QuanteraSXM; PHI Co.), binding energy of phosphorus atoms in the positive composite electrode using Li_{1.2}PS_{1.3} was larger than that of elemental phosphorus of around 130 eV (**Fig. S2**). This suggests that

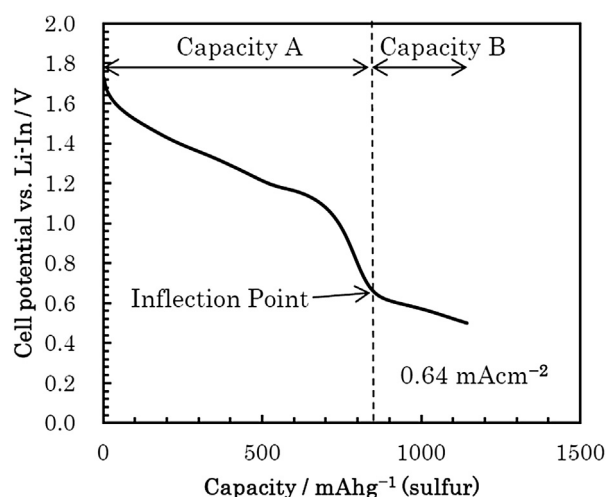


Fig. 3. Discharge curve of the all-solid-state Li/S cell for a positive composite electrode using Li_{1.2}PS_{1.3} under 0.64 mA cm⁻² at 25 °C. Capacity from 0 to the inflection point is denoted as “Capacity A” and that from the inflection point to the end point is denoted as “Capacity B”.

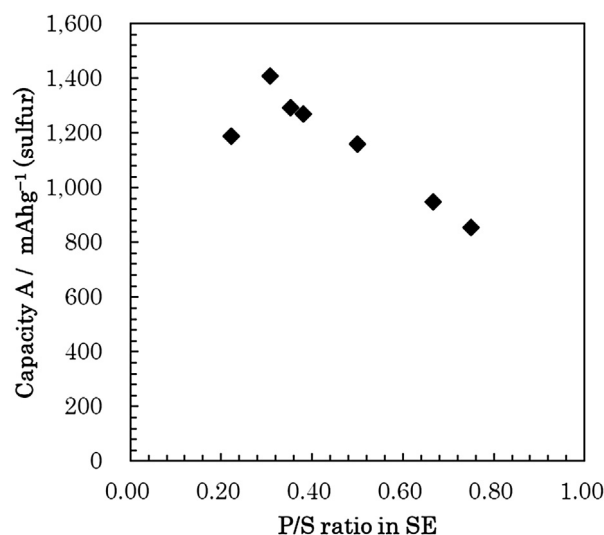


Fig. 4. Plot of the capacity of Capacity A for the P/S ratio of solid electrolyte (SE) in positive composite electrodes.

the valence of phosphorus atoms had increased. Therefore, we presume that the reaction occurs between phosphorus sulfides and lithium. **Fig. 4** shows the relationship between Capacity A and the P/S ratio in the SE, and **Fig. 5** shows the relationship between Capacity B and the P/S ratio in the SE. Capacity A decreases as the P/S ratio in the SE is increased, except for Li_{4.0}PS_{4.5} (P/S ratio = 0.222) (**Fig. 4**). Capacity B increases almost linearly without exception (**Fig. 5**). It is considered that in the region of Capacity A, the number of sulfur atoms that can participate in the reaction during discharge decrease because of a reaction with the phosphorus atoms in the SE, i.e., the formation of phosphorus sulfides. As an exception, the positive composite electrode using Li_{4.0}PS_{4.5} with the lowest P/S ratio exhibits a lower Capacity A value because despite the high conductivity of Li_{4.0}PS_{4.5}, the reactivity of sulfur is lower; therefore, the utilization efficiency is also lower. For the positive composite electrode using Li_{1.5}PS_{3.3}, the all-solid-state Li/S cell shows a Capacity A value close to the theoretically estimated maximum. These

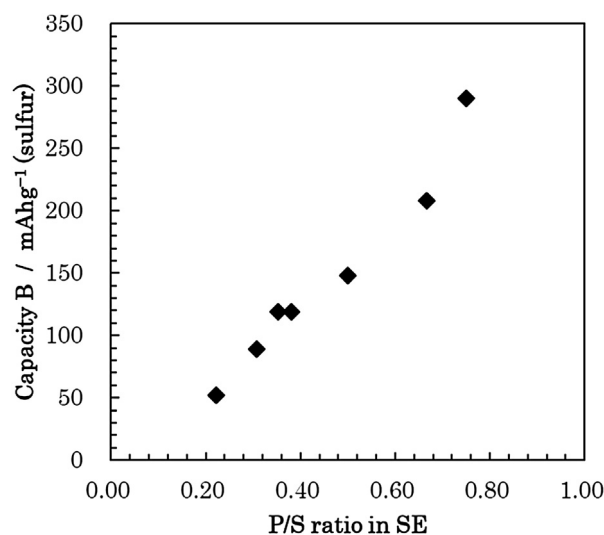


Fig. 5. Plot of the capacity of Capacity B for the P/S ratio of solid electrolyte (SEs) in positive composite electrodes.

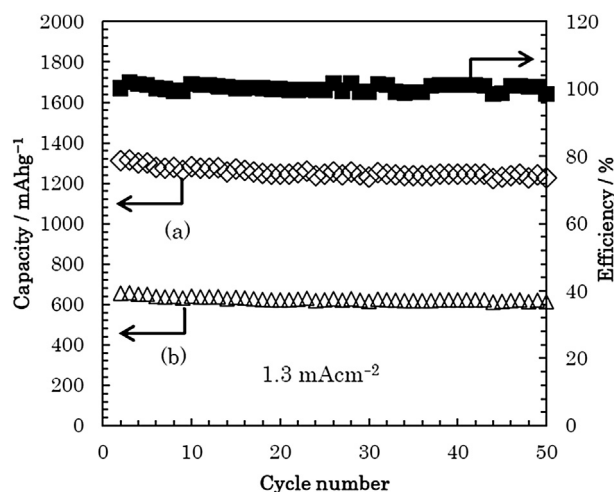


Fig. 6. Cycling performance of an all-solid-state Li/S cell with a positive composite electrode using $\text{Li}_{1.5}\text{PS}_{3.3}$ under 1.3 mA cm^{-2} at 25°C . The cut-off voltage was between 0.5 and 2.5 V (vs. Li–In). Capacity was normalized by weight of (a) sulfur and (b) positive composite electrode.

results might lead to the conclusion that the influence of the reactivity of sulfur on battery properties is more significant than ionic conductivity.

Fig. 6 shows the cycling performance of the all-solid-state Li/S cell in which the positive composite electrode uses $\text{Li}_{1.5}\text{PS}_{3.3}$ under 1.3 mA cm^{-2} (0.16 C) at 25°C . The coulombic efficiency is approximately 100% over 50 cycles. The cell exhibits excellent cycling performance. The capacity of the cell is greater than 1200 mAh g^{-1} (based on the incorporated sulfur active material weight) for 50 cycles, which corresponds to 600 mAh g^{-1} (based on the incorporated positive composite electrode weight, unless otherwise noted, the capacities hereafter are normalized to the sulfur active material content within the positive composite electrode).

Fig. 7 shows the discharge curve of the all-solid-state Li/S cell in which the positive composite electrode uses $\text{Li}_{1.5}\text{PS}_{3.3}$ and $\text{Li}_{4.0}\text{PS}_{4.5}$ under current densities of 0.64, 3.2, and 6.4 mA cm^{-2} (0.08, 0.4, and 0.8 C) at 25°C after full charge, and the cut-off voltage is 0.5 V (vs. Li–In). In this study, the electrode is approximately $50 \mu\text{m}$ thick,

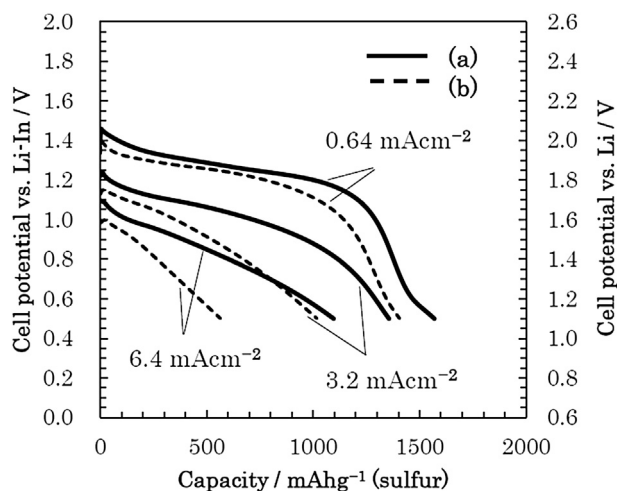


Fig. 7. Discharge curves of the all-solid-state Li/S cells with positive composite electrodes using (a) $\text{Li}_{1.5}\text{PS}_{3.3}$ and (b) $\text{Li}_{4.0}\text{PS}_{4.5}$ under current densities of 0.64, 3.2, and 6.4 mA cm^{-2} at 25°C . The cut-off voltage was 0.5 V (vs. Li–In).

which is sufficient for practical use. Nevertheless, the positive composite electrode using $\text{Li}_{1.5}\text{PS}_{3.3}$ always has larger capacity and higher discharge potential under all current densities investigated, despite having lower ionic conductivity than that using $\text{Li}_{4.0}\text{PS}_{4.5}$. The difference in capacity and discharge potential between **Fig. 7(a)** and (b) is more significant as current density increases. This indicates that the influence of the reactivity of sulfur is greater than that of ionic conductivity in the SE, which supports the speculation based on the data presented in **Fig. 4**. The capacity per gram of sulfur in the positive composite electrode using $\text{Li}_{1.5}\text{PS}_{3.3}$ under 0.64 and 6.4 mA cm^{-2} is 1568 and 1096 mAh g^{-1} , respectively. In other words, the capacity per gram of positive composite electrode using $\text{Li}_{1.5}\text{PS}_{3.3}$ under 0.64 and 6.4 mA cm^{-2} is 784 and 548 mAh g^{-1} , respectively. This value is extremely large even under high current density. In addition, this positive composite electrode exhibits good rate performance.

4. Conclusions

Focusing on the reactivity of sulfur, the relationship between the P/S ratio in an SE and capacity and potential of an all-solid-state Li/S battery was investigated to improve battery performance. The following conclusions could be drawn. The P/S ratio in the SE in a positive composite electrode correlated strongly with the reactivity of sulfur. The influence of sulfur's reactivity was greater than that of ionic conductivity in the SE. Even when the thickness of the positive composite electrode was as large as $50 \mu\text{m}$, which is sufficiently thick for practical use, the capacity of 1096 mAh g^{-1} under 6.4 mA cm^{-2} was achieved using $\text{Li}_{1.5}\text{PS}_{3.3}$ as the SE. Enhancing the reactivity of sulfur is considered to be a new strategy to improve the performance of all-solid-state Li/S batteries.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.04.032>.

References

- [1] D. Peramunage, S. Licht, *Science* 261 (1993) 1029–1032.
- [2] X. Ji, L.F. Nazar, *J. Mater. Chem.* 20 (2010) 9821–9826.
- [3] R.D. Rauh, K.M. Abraham, G.F. Pearson, S.K. Surprenate, S.B. Brummer, *J. Electrochem. Soc.* 126 (1979) 523–527.
- [4] Y.X. Yin, S. Xin, Y.G. Guo, L.J. Wan, *Angew. Chem. Int. Ed.* 52 (2013) 13186–13200.
- [5] N. Machida, T. Shigemaustu, *Chem. Lett.* 33 (2004) 376–377.
- [6] A. Hayashi, T. Ohtomo, F. Misuno, K. Tadanaga, M. Tatsumisago, *Electrochem. Commun.* 5 (2003) 701–705.
- [7] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, *Nat. Mater.* 10 (2011) 682–686.
- [8] K. Minami, A. Hayashi, M. Tatsumisago, *J. Ceram. Soc. Jpn.* 118 (4) (2010) 305–308.
- [9] M. Nagao, A. Hayashi, M. Tatsumisago, *Electrochim. Acta* 56 (2011) 6055–6059.
- [10] M. Nagao, A. Hayashi, M. Tatsumisago, *J. Mater. Chem.* 22 (2012) 10015–10020.
- [11] M. Nagao, A. Hayashi, M. Tatsumisago, *Energy Technol.* 1 (2013) 186–192.
- [12] Z. Liu, Z. Liu, W. Fu, N.J. Dudney, C. Liang, *Angew. Chem. Int. Ed.* 52 (2013) 1–5.
- [13] Y. Nishio, H. Kitaura, A. Hayashi, M. Tatsumisago, *J. Power Sources* 189 (2009) 629–632.
- [14] K. Takada, N. Aotani, K. Iwamoto, S. Kondo, *Solid State Ionics* 86 (1996) 877–882.
- [15] M. Nagao, A. Hayashi, M. Tatsumisago, *J. Power Sources* 196 (2011) 6902–6905.